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# THE MINIMUM OF RESISTANCE AT HIGH PRESSURE.

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## Introduction.

The electrical resistance of most metals decreases with rising pressure, but there are about half a dozen whose resistance increases.[1] Two examples are known, *Cs* and *Ba*, in which the two types of behavior are combined in a single substance, that is, the resistance at first drops, passes through a minimum, and then rises again at higher pressures. In general, if the resistance is plotted against pressure, it will be found that whether resistance increases or decreases with pressure the curvature is always the same, namely convex toward the pressure axis. The possibility of such behavior as that of *Cs* and *Ba* with their minimum resistance is evidently consistent with the common direction of curvature of all the curves. It was therefore natural to ask whether the minimum of resistance would not be found to be characteristic of all metals if pressure could only be pushed high enough. It is natural to look for this effect first in rubidium, the next most compressible metal after caesium; in fact, an extrapolation of the experimental values beyond the pressure range of the previous experiments, which was 12,000 kg., indicated that such a minimum was not impossible within a realizable pressure range. This paper contains an account of the actual attaining of the suspected minimum of rubidium with a new apparatus capable of reaching about 20,000 kg., of very definite indications of such a minimum for potassium at a pressure of 23,500 kg., 3500 kg. beyond that actually reached, and of new measurements on sodium to 18,000 kg., which indicate by extrapolation a minimum near 28,000 kg. In addition, the previous measurements on bismuth are extended to 50% beyond the previous maximum with no change in the trends previously found.

Two new pieces of apparatus were made for the higher pressure range. They were so much like the conventional apparatus of all my high pressure work that no extended description is necessary. Ordinarily there are two pressure cylinders, an upper one in which pressure is produced by the motion of a plunger, and a lower cylinder, connected to the upper one with a heavy pipe, in which is placed the particular substance to be investigated. The connecting pipe and the consequent large volumes are a disadvantage of this type of apparatus when attempting very high pressures. The new apparatus was therefore made in a single piece, being essentially the conventional upper cylinder, made longer than usual so that there was room in the bottom part for the resistance specimen. It is practically the same sort of thing that I used many years ago in measuring the transitions of ice up to 21,000 kg.[2]

The cylinders were of chrome vanadium steel, heat treated and subjected to several seasoning applications of 25,000 to 30,000 kg. in the usual way. The first cylinder was used for all the measurements except those on sodium. It is probable that a flaw was developed in this cylinder by the seasoning process, because a number of times there were leaks for which no adequate explanation appeared. This sort of behavior is the usual preliminary to the ultimate development of a well defined crack. Such a crack did not appear during this work, however, and at the expense of considerable trouble and a number of repetitions, enough runs were obtained without leak to give the information desired.

The second cylinder, that used with sodium, was given a preliminary seasoning like the first, and then, because of press of other work, was laid aside for about six months before making the actual measurements. The maximum pressure reached during the measurements with this was 18,000 kg.; here the steel stretched so much that higher pressures could not be reached, and this in spite of the fact that the initial seasoning had been made to nearly 30,000 kg. That is, the internal stress distribution produced by the original heavy overstrain gradually decays with time, and the elastic limit sinks toward the original value. This is in line with my previous experience, but I was not prepared for so large an effect. It is evident that in order to reach the highest pressures the measurements must be made as soon as possible after the preliminary treatment, and only a short life can be expected for the apparatus. The data obtained for sodium with this cylinder up to 18,000 indicated that the expected minimum would be beyond the range possible with this grade of

steel, so that it did not seem worth while to construct a new cylinder for the comparatively small increase of range that would have been possible.

In order to maintain temperature constant, the lower end of the hydraulic press as well as the cylinder itself had to be placed in the temperature bath.

A special three terminal insulating plug was made for this experiment, the depth of the mica washers being 50% greater than normal. The additional friction of the washers against the steel walls due to their additional depth provides an additional element of strength. The manganin gauge with which pressure was measured was wound from the same spool of wire as the standard gauge, and was calibrated by direct comparison with the standard. The resistance was only 25% of the standard, and for that reason the sensitiveness of the pressure readings was not so great as usual, but nevertheless the sensitivity was great enough to correspond to the accuracy of the calibration of the standard. It is to be remembered that the original calibration of the manganin by means of an absolute gauge covered a pressure range of only 13,000 kg.,[3] so that measurements beyond 13,000, which must be made by linear extrapolation, are not so certain as the measurements below 13,000. In view of the smallness of the coefficient of the manganin the uncertainty from this extrapolation is probably low. In any event, a small error in the gauge beyond 13,000 can only affect the pressure of the minimum and not the existence of the minimum itself, which was the point of chief interest in this investigation.

There follows now the detailed presentation of data.

## Detailed Data.

*Rubidium.*—The same metal which had been used in previous measurements and which had been purified by slow fractional distillation,[4] was used again. It had been kept sealed in glass under nujol since the previous measurements. It was extruded to a diameter of about 1.6 mm. and bent into a hairpin 5 or 6 cm. on a side. The potential and current terminals were, as before, fine wires of silver pierced through the rubidium wire and pinched into contact with it. The hairpin was mounted in a glass tube filled with nujol, the terminals were carried over the mouth of the tube and bent back over the outside, and the whole thing attached to a holder carried by the three terminal plug and thrust as a single assembly into the high pressure cylinder. Immediately before assembling in the cylinder the nujol

was flushed out and completely replaced with petroleum ether; this was necessary because the viscosity and freezing point of the transmitting liquid must both be low in order to transmit high pressure.

In addition to a number of unsuccessful runs, three runs were made which yielded satisfactory measurements. The first, at 30°, was to a maximum pressure of 17,800 kg., it being impossible to get higher because of leak. This run disclosed a remarkable flattening of the curve of resistance against pressure, so that it seemed highly probable that a maximum was near. The second run reached a maximum of 19,350 kg., where there was a slow leak. This run disclosed a minimum with both increasing and decreasing pressure, the best value for the location of the minimum being 17,900 kg. The discrepancy between readings with increasing and decreasing pressure on this run was so large, however, amounting to about 2.3% of the resistance at the minimum, that improvement seemed desirable. The discrepancy between ascending and descending readings is doubtless due in most part to the chemical action between the transmitting medium and the rubidium; a similar effect has been found in all my previous measurements of the resistance of the alkali metals when the metal has been used in the form of a bare wire. Another explanation of the discrepancy which might seem plausible is hysteresis due to internal strains, but the direction of the hysteresis is in the wrong direction to admit this explanation. In the effort to diminish the discrepancy as far as possible, the petroleum ether with which pressure was transmitted in the third set-up was made as chemically inert as possible by standing in contact with metallic sodium for a number of days before the run. The maximum pressure reached on the third run was 19,800 kg., where there was a slow leak. Again a minimum was found with increasing and decreasing pressure. The discrepancy between the ascending and descending points was now of the order of 1% of the resistance at the minimum; in general the points were much more regular than those of the second run, and were satisfactory enough.

The experimental points of the third run are shown in Figure 1. The points obtained with increasing pressure are doubtless to be preferred to the descending points, since the time during which chemical action may occur is less for these points. The relative resistances between 12,000 and 20,000 kg. at convenient pressure intervals, obtained from the increasing readings, are shown in Table I. A check on these readings is afforded by the readings previously obtained up to 12,000. These previous readings were made at 0° and 35°; by linear interpolation the relative resistance at 30° and

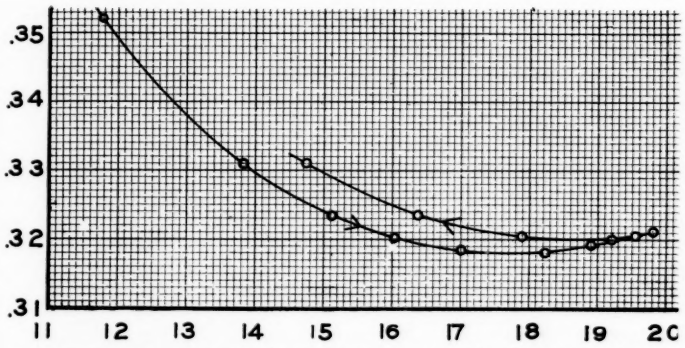


FIGURE 1. The measured relative resistance at 30° of rubidium against pressure in thousands of kg./cm.² as abscissas.

12,000 kg. is found to be 0.340, against 0.349 found now, a difference of 2.6%. The previous value is probably to be preferred, the difference being in the direction to indicate greater chemical action in the present experiment.

TABLE I.

RELATIVE RESISTANCE OF RUBIDIUM AT 30°, FROM THE SMOOTH CURVE THROUGH THE POINTS OBTAINED WTIH INCREASING PRESSURE OF THE PRESENT EXPERIMENT.

| Pressure kg./cm.² | $R/R_0$ |
|---|---|
| 12,000 | .3490 |
| 14,000 | .3295 |
| 16,000 | .3202 |
| 17,000 | .3184 |
| 18,000 | .3180 |
| 19,000 | .3194 |
| 20,000 | .3220 |

In Table II is shown the relative resistance at 30° at 1,000 kg. intervals up to 20,000 kg., to three significant figures. Up to 12,000 this table was constructed by linear interpolation between the previous values for 0° and 35°. Above 12,000, the values were obtained by applying a correction of 2.6% to the values of Table I, making a slight readjustment in the neighborhood of 12,000 to secure smooth first differences.

TABLE II.

MOST PROBABLE RELATIVE RESISTANCES OF RUBIDIUM AT 30°, OBTAINED BY COMBINING PREVIOUS AND PRESENT EXPERIMENTS.

| Pressure kg./cm.² | $R/R_0$ |
|---|---|
| 0 | 1.000 |
| 1,000 | .819 |
| 2,000 | .702 |
| 3,000 | .619 |
| 4,000 | .555 |
| 5,000 | .504 |
| 6,000 | .463 |
| 7,000 | .430 |
| 8,000 | .403 |
| 9,000 | .381 |
| 10,000 | .364 |
| 11,000 | .350 |
| 12,000 | .338 |
| 13,000 | .328 |
| 14,000 | .321 |
| 15,000 | .316 |
| 16,000 | .312 |
| 17,000 | .310 |
| 18,000 | .310 |
| 19,000 | .311 |
| 20,000 | .314 |

The most important result is that at 30° the resistance of rubidium passes through a minimum at 17,000 kg., where the resistance is 0.310 of its value at atmospheric pressure at the same temperature. This may be compared with the corresponding result for caesium, which at 0° has a minimum of 4,200 kg. of about 0.71 the initial resistance.

*Potassium.*—Although in view of the very large increase of the pressure of the minimum on passing from caesium to rubidium it appeared highly improbable that the pressure of the minimum of potassium, granting that it exists, could actually be reached with this apparatus, nevertheless the additional information to be obtained by extending the pressure range by 60% might be expected to give valuable information as to the probable existence and location of such a minimum.

The experimental set-up was practically the same as for rubidium.

The material was from the same original batch as that on which my previous determinations of the effect of pressure on melting point, resistance, and compressibility were made;[5] it has been kept in the meantime sealed in glass under nujol. The readings, which are shown in Figure 2, were very regular, there being very little difference

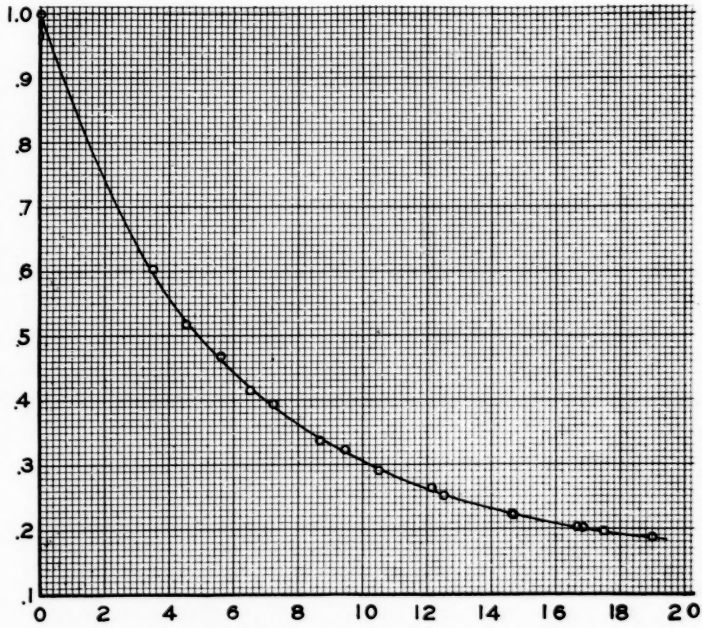


FIGURE 2. The measured relative resistance at 30° of potassium against pressure in thousands of kg./cm.² as abscissas.

between the ascending and descending branches. It is to be expected that any discrepancy between ascending and descending points would be much less in this case than for rubidium, both because potassium is less active chemically than rubidium, and because it is not so soft mechanically.

A fairly good check on the new results can be obtained by comparing with the previous measurements on potassium to 12,000 at 0°.

The present value for the relative resistance at 12,000 is 0.261, compared with 0.271 of the previous measurements. The difference, which is small, is in the right direction, and of a not unreasonable magnitude to be accounted for by the temperature difference. The previous measurements were made on potassium at only one temperature, so that a temperature interpolation could not be made such as was possible for rubidium.

The relative resistances in terms of the resistance at atmospheric pressure at 2000 kg. intervals up to 20,000 at 30° are shown in Table III.

TABLE III.

| Pressure kg./cm.² | Relative Resistances of Potassium at 30° |
|---|---|
| 0 | 1.000 |
| 2,000 | .734 |
| 4,000 | .557 |
| 6,000 | .443 |
| 8,000 | .362 |
| 10,000 | .305 |
| 12,000 | .262 |
| 14,000 | .231 |
| 16,000 | .208 |
| 18,000 | .192 |
| 20,000 | .181 |

The minimum is seen to lie beyond 20,000. Direct extrapolation of the curve of resistance against pressure in order to find the minimum would not be accurate; this may be better done by plotting the first differences against pressure. In Fig. 3 the differences of relative resistance for 2000 kg. intervals are plotted against the mean pressure of the intervals. This curve is so nearly linear at the high pressure end that it can be extrapolated with little uncertainty. The curve is seen to cross the axis at about 23,500 kg., which may therefore be taken to be the pressure of the minimum. The minimum relative resistance calculated from the extrapolated first differences is 0.175. The pressure of the minimum is thus not so high as might have been anticipated from the relatively large increase in the pressure of the minimum on passing from caesium to rubidium.

*Sodium.*

The specimen was formed and treated in the same way as *Rb* and *K*. The material was from the same batch as that whose pressure

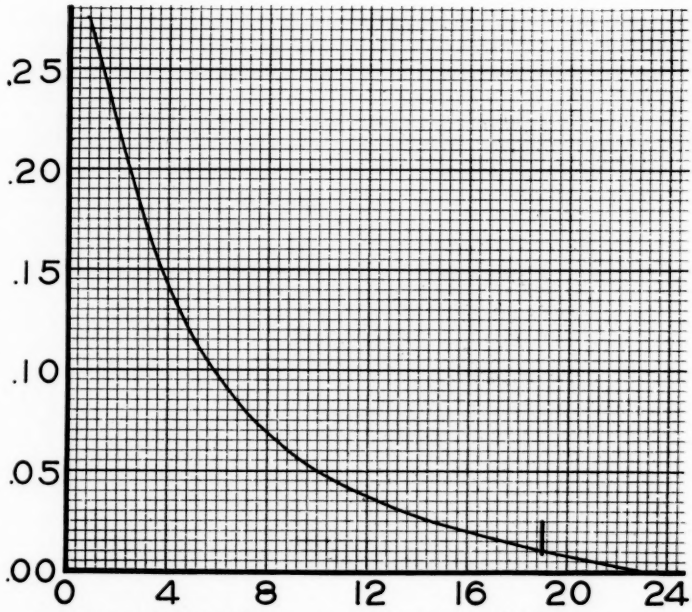


FIGURE 3. The first differences of relative resistance for 2000 kg. intervals of potassium plotted against pressure in thousands of kg.cm.$^2$ as abscissas.

coefficient of resistance and melting curve under pressure were previously measured,[6] and which gave evidence of high purity by the sharpness of the freezing point. It has been kept since that time in a glass stoppered jar under kerosene. There has been some surface action with the kerosene, but the piece used was cut from the interior of a large block, and should be as pure as the original.

Measurements were made at 30° in the second cylinder; as already explained, the cylinder stretched so much beyond 18,000 kg. that readings could not be obtained at higher pressures. The measured relative resistances are plotted in Fig. 4. There is considerable difference between the ascending and descending readings at the lower pressures, which becomes much smaller beyond 10,000 kg. It is uncertain how much of this is due to chemical action and how much to mechanical distortion. If the mean of the two zero readings

is taken as most probably correct, it will be found that the relative resistance at 12,000 kg. is .4210 against .4245 previously found. The difference is only 0.82%. It is probable that the previous values

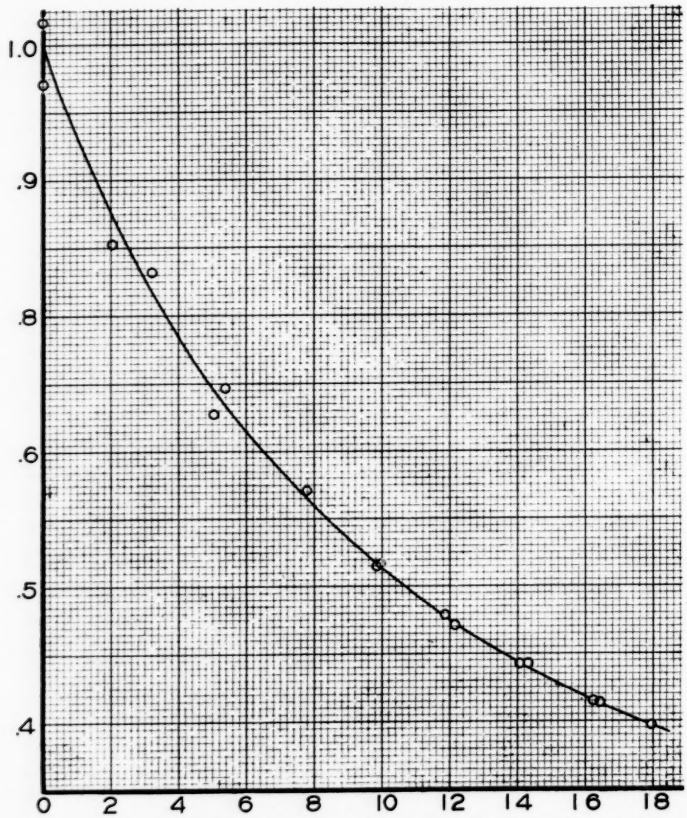


FIGURE 4. The measured relative resistance at 30° of sodium against pressure in thousands of kg./cm.$^2$ as abscissas.

are to be preferred, since more attention was then paid to the low pressure behavior. Agreement between the two sets of data at

12,000 can be obtained by assuming that the proper zero of these measurements is not the mean of the two observed zeros, but about 0.3% higher. The smooth curve in Fig. 4 has been drawn in accordance with this adjustment.

The relative resistances at 1,000 kg. are shown in Table IV. The four significant figures given are justified by the data, and it is in fact necessary to retain this number of figures to obtain smooth first differences. Compared with the previous results at 12,000 the maximum difference is 3 in the third figure at 4,000 and 5,000, and the average difference 1.

TABLE IV.

| Pressure kg./cm.² | Relative Resistances of Sodium at 30° |
|---|---|
| 0 | 1.0000 |
| 1,000 | .9338 |
| 2,000 | .8770 |
| 3,000 | .8278 |
| 4,000 | .7850 |
| 5,000 | .7480 |
| 6,000 | .7156 |
| 7,000 | .6866 |
| 8,000 | .6601 |
| 9,000 | .6361 |
| 10,000 | .6141 |
| 11,000 | .5941 |
| 12,000 | .5757 |
| 13,000 | .5590 |
| 14,000 | .5442 |
| 15,000 | .5308 |
| 16,000 | .5185 |
| 17,000 | .5073 |
| 18,000 | .4974 |

In order to estimate whether there is a minimum resistance, the differences for 1,000 kg. intervals are plotted against pressure in Fig. 5. There can be little doubt that the curve will cross the axis, so that it is highly probable that *Na* has a minimum as well as *Cs*, *Rb* and *K*. The dotted extension of the curve in Fig. 5 fits smoothly with the experimentally determined part, shown as a full line, and indicates a minimum near 28,000 kg., with a minimum relative resistance of 0.442.

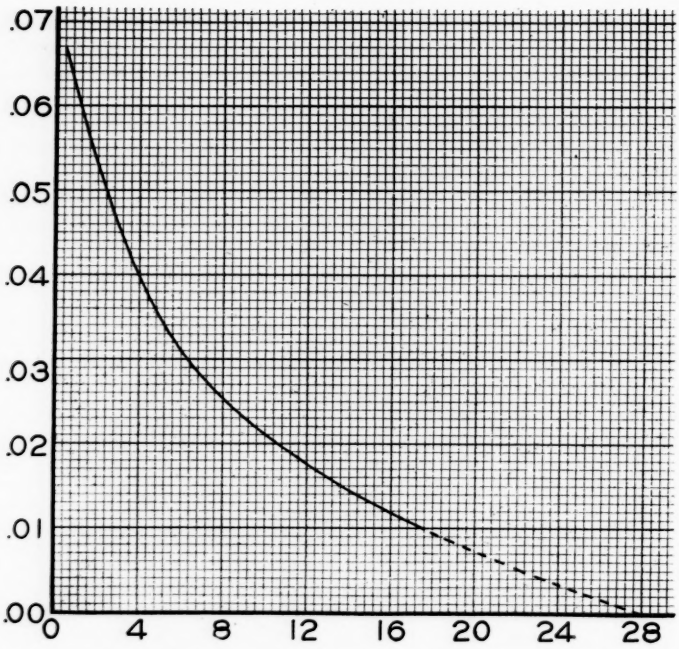


FIGURE 5. The first differences of relative resistance for 1000 kg. intervals of sodium plotted against pressure in thousands of kg./cm.$^2$ as abscissas.

*Bismuth.*

My particular reason for trying bismuth to higher pressures than formerly was that because of the abnormal increase of volume of bismuth on freezing it is to be expected that at sufficiently high pressures a new high pressure modification may exist, analogous to the high pressure forms of ice. Any such polymorphic transition should disclose itself by a discontinuity in the resistance.

The material was a single crystal rod of bismuth, with cleavage plane parallel to the length, from the same set of rods whose thermoelectric properties and resistance under pressure have been previously measured.[7] With this rod a single run was made to a maximum pressure of 18,400 kg. at 30°. The points lay perfectly smoothly,

with no perceptible difference between the ascending and descending points, and no indication whatever of any sort of discontinuity. The transition, if it exists, must therefore occur at pressure beyond 18,400, or else the transition was suppressed by internal viscosity.

Previously measurements have been made to 12,000 on a crystal with cleavage at 4° to the length, and the results represented by a second degree expression in the pressure. We have to ask in the first place whether the new results agree with the former ones over the common pressure range, and secondly whether the second degree expression may be used to extrapolate beyond 12,000. The formula gives for the relative resistance at 12,000 1.168, against 1.162 found now, and at 18,000 1.284, against 1.273 found now. The differences are thus small, and are in the direction to be accounted for by the slight difference in orientation. The present values may therefore be considered checked, and the use of the previous formulas by extrapolation up to 18,000, and presumably materially higher, is justified.

It is to be remarked that we have here also presumptive evidence of the legitimateness of extrapolating the manganin gauge calibration beyond 13,000. One method of checking such an extrapolation would be to find whether the same pressure is given by extrapolating with the formulas for two different metals; this is essentially what has been done here.

## Discussion.

The chief conclusion to be drawn from the results of this paper is that it is almost certain that ultimately, at sufficiently high pressures, the resistance of all the alkali metals increases under pressure. This increase has actually been realized for *Cs* and *Rb*, and *Li* already at atmospheric pressure increases in resistance; the extrapolation for *K* and *Na* is not a large one, and it seems practically certain that they also must ultimately increase in resistance.

It is natural to look for regularities in the minimum data on passing from metal to metal in the alkali series. It is evident in the first place that *Li* is entirely out of the sequence. This perhaps is not surprising in view of the very simple electronic structure of the atom of *Li*, compared with that of the others. Consider now the remaining four metals *Na*, *K*, *Rb*, and *Cs*; the essential data for them are collected in Table V. If the pressure of the minimum is plotted against atomic number, a fairly smooth curve will be obtained, the pressure of the minimum dropping at an accelerated rate in the direction of

*Cs*. If the relative resistance at the minimum is plotted against atomic number a parabolic curve will be found having a deep minimum at *K*. One is reminded of another respect in which *K* falls out of the sequence, namely in the very loose electronic structure of the atom and the surprisingly persistent compressibility at high pressures emphasized in a previous paper;[8] there does not, however, appear to be any very close correlation between these other effects and the behavior of resistance found here.

TABLE V.

| Metal | Atomic Number | Pressure at minimum | $\frac{R(\text{min.})}{R(\text{atoms.})}$ |
|---|---|---|---|
| *Na* | 11 | 28,000* | .442* |
| *K* | 19 | 23,500* | .175* |
| *Rb* | 37 | 17,800 | .310 |
| *Cs* | 55 | 4,200 | .71 |

* Extrapolated.

The considerations of the introductory paragraph make it natural to suppose that the phenomena shown by the alkalies may be shown by all other metals at high enough pressures; we inquire at what pressures we might possibly find this effect. The alkali earth series is the most natural place to look next. Here barium does have the effect,[9] the pressure of the minimum being about 8600 kg. at 30°, and strontium and calcium[10] have a positive pressure coefficient already at atmospheric pressure like lithium. Beryllium,[11] however, the analog of lithium, has a normal negative coefficient, and magnesium[12] the analog of sodium, also has a negative coefficient. The resistance of *Be* and *Mg*, when plotted against pressure, shows curvature in a direction consistent with a minimum at higher pressures, as do all other metals, and the pressure of the minimum indicated by extrapolation of the second degree formula valid up to 12000 kg. is 46,000 kg. for *Be* and 49,000 for *Mg*. But a second degree formula almost certainly gives by extrapolation too low a pressure for the minimum, as shown by Figures 3 and 5, which would be straight lines if a second degree formula were valid. It is therefore evident that the possible minimum of *Be* or *Mg* is at a pressure so high that it is hopeless to try to reach it with present means, or even to get close enough to allow a secure extrapolation. Searching the rest of the measured elements, one would expect to find the effect most easily with the most compressible metals. Of these, thallium[13] gives by second degree extrapolation a pressure of 46,000 kg. and

indium[14] 37,000, which again is certainly too low in view of the detectible departures from the second degree relation below 12,000. It would appear therefore that the only chance of finding the effect in the pressure range at present attainable is with some metal not yet investigated. The largest gap in the investigated metals is in the rare earths: here only a few have been measured, but they are not encouraging. Perhaps the most promising candidates are scandium and yttrium, but these have not yet been produced in sufficiently large quantities in the metalic condition.

The fact that bismuth and antimony have positive pressure coefficients of resistance in the ordinary range requires brief comment. In spite of the fact that the curvature of the plot of resistance against pressure is the same as that of the alkali metals and earths, it is not unlikely that the mechanism of the positive pressure coefficient is different in the two cases. In *Bi* and *Sb* the mechanism is probably special, connected in some way with the crystal structure, as shown by the fact that the coefficient of liquid *Bi* is negative.[15] The positive coefficient of the alkali metals and earths is probably more intimately connected with the structure of the atom, as shown by the fact that the coefficient of liquid as well as solid *Li*[16] is positive. It was shown in a previous paper[17] that it is highly probable that the coefficient of liquid *Cs* will also be positive at pressures high enough, and by analogy, one would expect similar behavior for the other alkali metals.

In speculations as to possible behavior at very high pressures, a significant feature of the behavior of *Cs* should be kept in mind. If the "instantaneous" pressure coefficient $\frac{1}{R}\left(\frac{\partial R}{\partial p}\right)_t$ of *Cs* is plotted against pressure, a curve will be obtained which crosses the axis at 4200 kg., the pressure of the minimum, and which in the low pressure range is rather strongly concave upward, so that a wide extrapolation might be taken to indicate a second crossing of the axis, with a maximum, which would mean that at pressures still higher the pressure coefficient of resistance would again become negative. But this extrapolation is not valid because of a reversal of the direction of curvature of $\frac{1}{R}\left(\frac{\partial R}{\partial p}\right)_t$, that is, a reversal of the third pressure derivative, above 8,000, so that above 8,000 kg. the pressure coefficient becomes increasingly positive, and there is no indicated possibility of a return to normal behavior at excessively high pressures. This has application to the other alkali metals; their third derivatives

are such as not to make impossible a second reversal at exceedingly high pressures, but judging by the analogy of *Cs*, this initial possibility will be eliminated at high pressures, and there is no reason to think that the resistance of all these metals will not continue to increase at an ever accelerated pace at pressures far beyond the present experimental range.

The theoretical significance of the reversal of the pressure coefficient at high pressures is at present obscure; there does not seem to be any suggestion of such a phenomenon in the present wave-mechanics pictures of the mechanism of resistance. This must nevertheless be important not only for theories of resistance, but for theories of the structure of the atom, since we have here definite evidence of a reversal in ordinary atomic properties produced by forces which are not high in comparison with the forces between different electrons in the same atom. It may well be that there is here a possibility of obtaining by direct experiment some inkling of atomic behavior under certain stellar conditions.

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